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Effects of additives on mechanical and barrier properties of polyhydroxyalkanoate-derived bionanocomposite films by solution casting

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Polyhydroxyalkanoates are naturally occurring, non-toxic aliphatic polyesters. Nanocomposite fabrication is an effective and cost-efficient approach to modulate polymer properties. Within the scope of this study, poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB)/poly(3-hydroxybutyrate) (P3HB) (PHAs) bioblends were developed by using solution casting and extrusion methods. The optimum compositions of PHAs bioblends were determined as 80% P3HB4HB for solution casting method and 60% P3HB4HB for extrusion method. To obtain PHAs-based bionanocomposites, two types of copper-based metal organic frameworks (CuMOF and GO@CuMOF) nanocrystals (0.5; 1.0 wt% and 0.1; 0.5 wt%), and bentonite, sepiolite, high-purity sepiolite (1; 2; 3 wt%) nanoclays were added to the PHAs bioblend matrix. The effects of nanofillers on mechanical and optical properties, barrier performance and thermal behavior of bionanocomposites were investigated. When the mechanical properties of bionanocomposites obtained by the solution casting method were examined according to the polyethylene reference, the optimum ratio of all nanoclays was 3% while the optimum ratios of CuMOF nanocrystals were 1 and 0.1, respectively. PHAs/HPS-3 bionanocomposite films showed a 62.5% improvement in oxygen transmittance rate (OTR) compared to the flexible polyethylene reference. Material properties were recognized through solution casting studies, and it was determined that bionanocomposites have gained good qualities for flexible packaging with the use of CuMOF and high-purity sepiolite (HPS) nanofillers.

Keywords: Polyhydroxyalkanoate, solution casting, extrusion, bioblend, high-purity sepiolite

INTRODUCTION

Traditional plastics ensure perfect functionality for use as flexible packaging materials, possessing mechanical and barrier properties in concur with low production costs [1]. Use of biopolymers in the sustainable packaging industry has shown intense progress because of recent trends in the market moving toward green packaging, recyclability and waste reduction [2]. Sustainability is vital as it encourages politics, industry and academia to develop sustainable and circular alternatives to preserve resources by focusing on biopolymers [3]. Biopolymers are polymers which include convalently bonded monomeric units, to compose chain-like molecules. Biopolymers are renewable and have, therefore, the capability to be degraded through the action of naturally occurring organisms leaving behind environmentally harmless organic by-products such as CO_2 and H_2O [4]. Polyhydroxyalkanoates (PHAs) are produced in nature by bacterial fermentation. Depending on the carbon atoms, PHAs are classifed in three groups: short-chain length PHAs (sCLPHAs) (4 to 6 carbon atoms), medium-chain length PHAs (mCL-PHAs) (more than six carbons), and long-chain length (lCL-PHAs) (more than 14 carbons) [5]. Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P3HB3HV), poly(3-hydroxybutyrate) (P3HB), polyhydroxyhexanoate (PHH) and polyhydroxyoctanoate (PHO) are widely used copolymers of PHAs. P3HB, P3HB4HB and P3HB3HV are the most popular among them [5]. In the study conducted by Vostrejs and his team in 2020, they intended to research the thermal, mechanical and gas permeability properties of crystalline PHB blended with amorphous PHA, to determine the effect of grape seed lignin association on thermal and mechanical properties of PHB/PHA blends and to assess the antibacterial effect of grape seed lignin associated in PHB/PHA films [6]. Within the scope of this study, a solution casting method and extrusion methods were employed to prepare P3HB4HB/PHB bioblends using a plasticizer (Joncryl® ADR4468). After the determination of optimum bioblend composition, P3HB4HB/PHB bionanocomposites were prepared with copper-based metal organic framework (CuMOF) and GO@CuMOF hybrid nanocrystals and different nanoclay types (bentonite, sepiolite, high-purity

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sepiolite). CuMOF nanocrystals were synthesized by the solvothermal synthesis method known as MOF199 or HKUST-1 [7]. While bentonite and sepiolite have a layered structure, high-purity sepiolite has a needle-point structure. The effects of nanofillers on mechanical and optical properties, barrier performance and thermal behavior of biocomposites were investigated.

EXPERIMENTAL

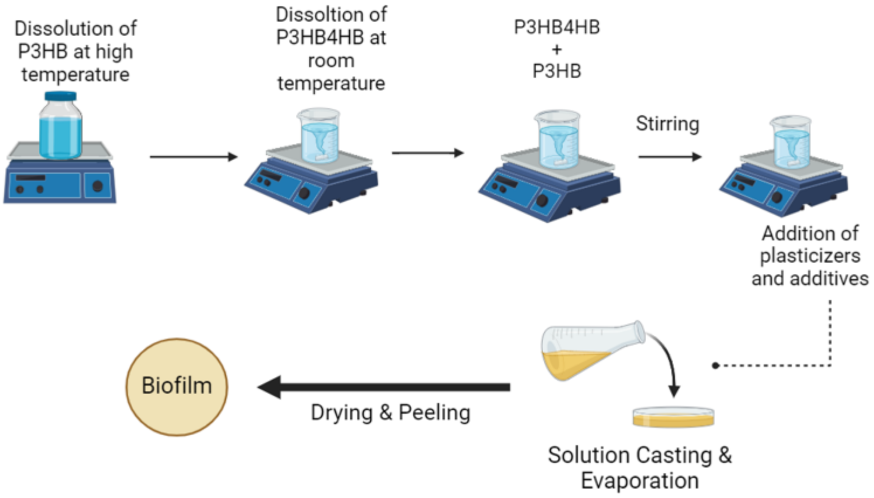
In the preparation of bionanocomposite films by solution casting method, firstly various ratio studies of P3HB4HB/P3HB (PHAs) in different composition (50:50; 60:40; 70:30; 80:20 wt%) were carried out with plasticizer (J; Joncryl® ADR 4468), and the optimum ratio of PHAs bioblends was determined. By adding metal organic frameworks based nanofillers (0.1; 0.5; 1%) and different nanoclay types (1; 2; 3%) into PHAs bioblend, bionanocomposites were prepared and subjected to characterization tests. The solution casting method is shown in Scheme 1.

In extrusion studies, after obtaining PHAs granules with different ratios in a twin-screw extruder then bioblends were produced by blown film extrusion. The optimum bioblend composition and operating parameters have been determined. Extrusion studies continued by adding 3% high purity sepiolite to the PHAs bioblend structure. The mechanical, optical, barrier and thermal properties of the PHAs/HPS-3 bionanocomposite were examined.

MATERIALS

Preparation of bioblend films

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB) was supplied from CJ Biomaterials Co., Ltd. Poly(3-hydroxybutyrate) (P3HB) was purchased from Helian Polymers Co., Ltd. Joncryl® ADR 4468 (J) was accommodated from "BASF" company and used as plasticizer. Chloroform was provided from Interlab Co., Ltd. Bentonite (B), sepiolite (S) and high purity sepiolite (HPS) were supplied from Tolsa.



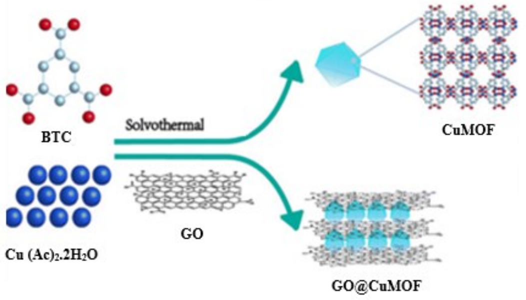
Scheme 1. Schematic representation of the solution casting method

Fig. 1. Images of PHAs bioblend granules and blown film production

Synthesis of CuMOF and GO@CuMOF nanocrystals

1,3,5-Benzenetricarboxylic acid (BTC) was obtained from "Analitik Kimya" company. Copper acetate ($Cu(Ac)_2.2H_20$) and triethylamine (TEA) were supplied from "Acros Organics" company. N,N-Dimethylformamide was obtained from "Tekkim" company. Ethanol was provided by "Sigma Aldrich" company. Graphene oxide (GO) was purchased from "Aerofen" company.

CuMOF nanocrystals were synthesized in the laboratory under room conditions by the solvothermal synthesis method, known as MOF199 or HKUST-1 [7].



Scheme 2. Schematic representation of the synthesis of CuMOF and GO@CuMOF hybrid nanocrystals [8]

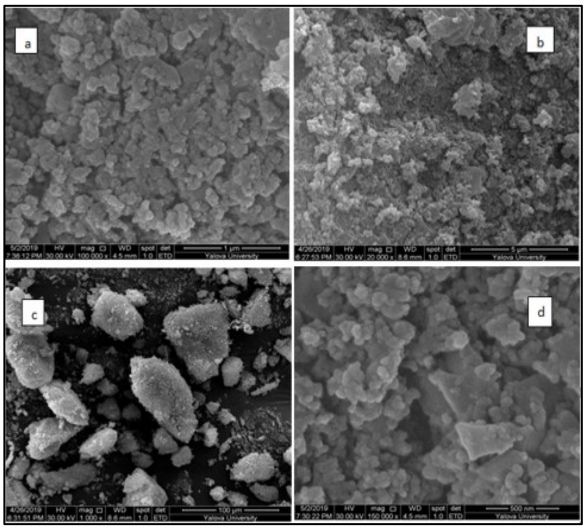


Fig. 2. SEM images of CuMOF nanocrystals (a:100000×; b:20000×; c:1000×; d:150000×)

It is seen from the SEM images the sizes of CuMOF nanocrystals were distributed in the range of 40-60 nm and there was aggregation in the synthesized CuMOF nanocrystals.

BET analysis results of CuMOF and GO@CuMOF nanocrystals - surface area, average pore volume and pore diameter values are shown in Table 1. The results show compatibility with the literature [9].

Table 1. BET analysis results of CuMOF and GO@CuMOF nanocrystals

Nanoparticles	BET surface area (m^2.g^{-1})	Average pore polume (cm^3.g^{-1})	Average pore diameter (nm)
CuMOF	1322.96	0.42	3.17
GO@CuMOF	227.21	0.12	0.32

Chemical composition and notation of P3HB4HB/P3HB (PHAs) bioblends by solution casting method are given in Table 2.

RESULTS AND DISCUSSION:

Preparation of PHAs bionanocomposite films with solution casting method

Mechanical, optical, barrier and thermal characteristics of PHAs bionanocomposites were examined. Mechanical properties of PHAs bioblends prepared with different ratios by solution casting method are shown in Table 3. When various pure and plasticizer containing bioblends were examined, it was determined that the optimum blend ratio was PHAs (80/20) compared to the reference polyethylene. Table 4 shows that the optimum usage rates of CuMOF and GO@CuMOF nanocrystals are 1% and 0.1%, respectively. In Table 5, the optimum nanoclay rates for bentonite, sepiolite and high purity sepiolite were determined as 3% compared to reference polyethylene.

Optical and barrier properties of PHAs bionanocomposites prepared by solution casting method are given in Table 6. The gloss value increased with the compatibility between the two biopolymers and the increase in the ratio of high purity sepiolite contribution. When the barrier results were evaluated, the inherently good OTR characteristics of PHA and PHB showed an improvement with the addition of CuMOF and high-purity sepiolite nanofillers compared to the reference polyethylene [10].

DSC curves of PHAs bionanocomposites are examined in Figure 3. It is seen that only CuMOF and HPS additives increased the bioblend crystallinity. Since polyethylene is a semi-crystalline raw material, the increase in crystallinity is a sign of the transition to flexible packaging.

Preparation of PHAs bionanocomposite films with extrusion

Mechanical, optical, barrier and thermal characterizations of the prepared biofilms were carried out. 100 µ polyethylene film was chosen as reference polyethylene.

Table 2. Chemical composition and notation of P3HB4HB/P3HB (PHAs) bioblends by solution casting method

Code	*P3HB4HB (wt.%)*	*P3HB (wt.%)*	*Plasticizer (J, wt.%)*	*Nanofiller (wt.%)*
P3HB4HB/P3HB	80	20	0	0
P3HB4HB/P3HB/J (PHAs)	80	20	1	0
PHAs/CuMOF-0.5	80	20	1	0.5
PHAs/CuMOF-1	80	20	1	1
PHAs/GO@CuMOF-0.1	80	20	1	0.1
PHAs/GO@CuMOF-0.5	80	20	1	0.5
PHAs/B-1	80	20	1	1
PHAs/B-2	80	20	1	2
PHAs/B-3	80	20	1	3
PHAs/S-1	80	20	1	1
PHAs/S-2	80	20	1	2
PHAs/S-3	80	20	1	3
PHAs/HPS-1	80	20	1	1
PHAs/HPS-2	80	20	1	2
PHAs/HPS-3	80	20	1	3

Table 3. Mechanical properties of PHAs bioblends prepared with different ratios by solution casting method

Bioblend Films (Thickness: 100±5 μ)	Tensile Strength (Mpa)	Elongation at Break (%)	E-Modulus (N/mm^2)
Polyethylene (Reference film)	24±2	322±2	283±3
P3HB4HB80P3HB20	8±2	468±2	193±3
P3HB4HB70P3HB30	9±2	120±3	346±2
P3HB4HB60P3HB40	12±1	204±1	494±4
P3HB4HB503PHB50	15±2	119±1	740±2
P3HB4HB80P3HB20/J	6±1	352±2	204±2
P3HB4HB70P3HB30/J	9±1	179±1	369±1
P3HB4HB60P3HB40/J	12±2	57±3	586±2
P3HB4HB50P3HB50/J	13±1	68±2	588±2

Table 4. Mechanical properties of PHAs/CuMOFs bionanocomposites by solution casting method

Bionanocomposite (Thickness: 100±5 μ)	Tensile Strength (Mpa)	Elongation at Break (%)	E-Modulus (N/mm^2)
Polyethylene (Reference film)	24±2	322±2	283±3
P3HB4HB/P3HB	8±1	468±2	193±3
PHAs	6±1	352±2	204±2
PHAs/CuMOF-0.5	7±1	319±1	230±1
PHAs/CuMOF-1	10±2	423±3	256±1
PHAs/GO@CuMOF-0.1	8±1	416±2	233±2
PHAs/GO@CuMOF-0.5	7±1	446±2	174±1

Table 5. Mechanical properties of PHAs/nanoclay bionanocomposites by solution casting method

Bionanocomposite Films (Thickness: 100±5 μ)	Tensile Strength (Mpa)	Elongation at Break (%)	E-Modulus (N/mm^2)
Polyethylene (Reference film)	24±2	322±2	283±3
P3HB4HB/P3HB	8±2	468±2	193±3
PHAs	6±1	352±2	204±2
PHAs/B-1	9±1	279±1	365±1
PHAs/B-2	8±2	270±3	304±1
PHAs/B-3	8±1	323±3	293±3
PHAs/S-1	7±1	274±2	287±2
PHAs/S-2	9±2	301±1	374±1
PHAs/S-3	8±1	224±1	341±1
PHAs/HPS-1	9±3	287±3	214±2
PHAs/HPS-2	9±1	299±1	238±3
PHAs/HPS-3	10±2	318±2	276±1

Table 6. Optical and barrier properties of PHAs bionanocomposites by solution casting method

Bionanocomposite Films (Thickness: 100±5 µ)	Gloss (60°) (%)	OTR (cc/m^2)
Polyethylene (Reference film)	77±3	408±3
P3HB4HB/P3HB	22±2	344±1
PHAs	28±3	325±2
PHAs/CuMOF-0.5	31±1	297±3
PHAs/GO@CuMOF-0.1	29±1	318±2
PHAs/B-3	33±3	338±2
PHAs/S-3	34±2	301±1
PHAs/HPS-3	37±3	286±1

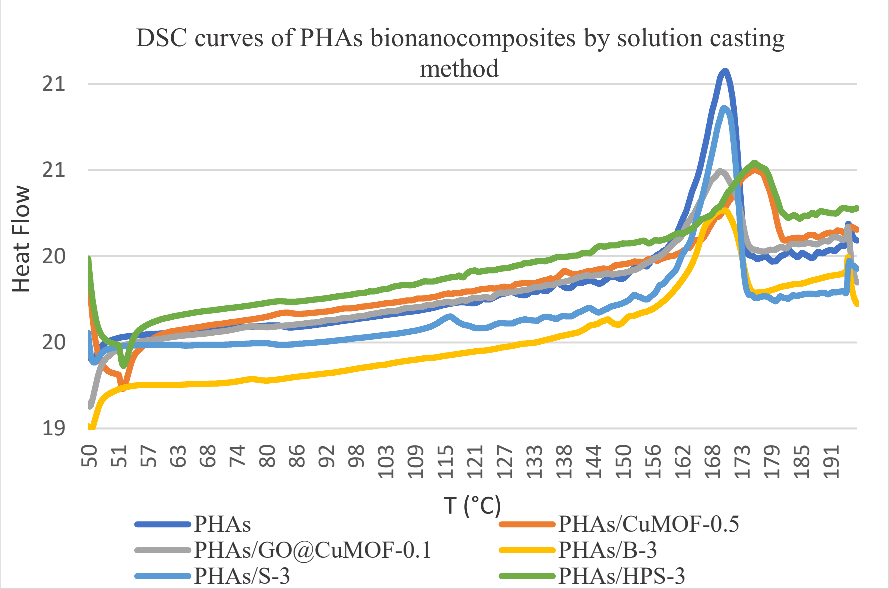


Fig. 3. DSC curves of PHAs bionanocomposites by solution casting method

Table 7. Mechanical properties of PHAs bioblends prepared with different ratios by extrusion method

Bioblend Films (Thickness: 100±5 µ)	Tensile Strength (Mpa)	Elongation at Break (%)	E-Modulus (N/mm^2)
Polyethylene (Reference film)	24±2	322±2	283±3
P3HB4HB50/P3HB50	9±1	804±1	377±2
P3HB4HB55/P3HB45	10±2	797±3	354±4
P3HB4HB60/P3HB40	11±1	789±1	346±2
P3HB4HB50P/3HB50/J	12±2	802±2	339±1
P3HB4HB55/P3HB45/J	12±2	813±3	326±3
P3HB4HB60/P3HB40/J	14±1	822±2	313±2

Mechanical properties of PHAs bioblends prepared with different ratios by extrusion method were given in Table 7. When various pure and plasticizer bioblend studies were examined compared to reference polyethylene, it was determined that the optimum composition of PHAs bioblend by extrusion method was as 60% of P3HB4HB and 40% of P3HB in presence of plasticizer.

Mechanical properties of PHAs/nanoclay bionanocomposites by extrusion method are shown in Table 8.

When the mechanical properties were evaluated according to bionanocomposites containing high purity sepiolite, it was determined that the optimum nanoclay usage rate was 3%.

Optical and barrier properties of PHAs bionanocomposites by extrusion method were given in Table 9. The gloss value increased with the compatibility between the two biopolymers and the increase in the ratio of high purity sepiolite contribution. Adding 3% HPS to PHAs bioblend, whose components have good OTR values on their own, improved the OTR value [10].

Table 8. Mechanical properties of PHAs/nanoclay bionanocomposites by extrusion method

Bionanocomposite Films (Thickness: 100±5 µ)	Tensile Strength (Mpa)	Elongation at Break (%)	E-Modulus (N/mm^2)
Polyethylene (Reference film)	24±2	322±2	283±3
P3HB4HB60/P3HB40	11±1	789±1	346±1
P3HB4HB60/P3HB40/J (PHAs)	14±2	822±2	313±3
PHAs/HPS-1	9±1	566±3	322±2
PHAs/HPS-2	10±1	403±3	318±3
PHAs/HPS-3	12±2	387±2	306±1

Table 9. Optical and barrier properties of PHAs bionanocomposites by extrusion method

Bionanocomposite Films (Thickness: 100±5 µ)	Gloss (60°) (%)	OTR (cc/m^2)
Polyethylene (Reference film)	77±3	408±3
P3HB4HB60/P3HB40	24±2	302±2
PHAs	28±3	287±3
PHAs/HPS-1	34±2	258±2
PHAs/HPS-2	39±1	245±1
PHAs/HPS-3	48±3	225±1

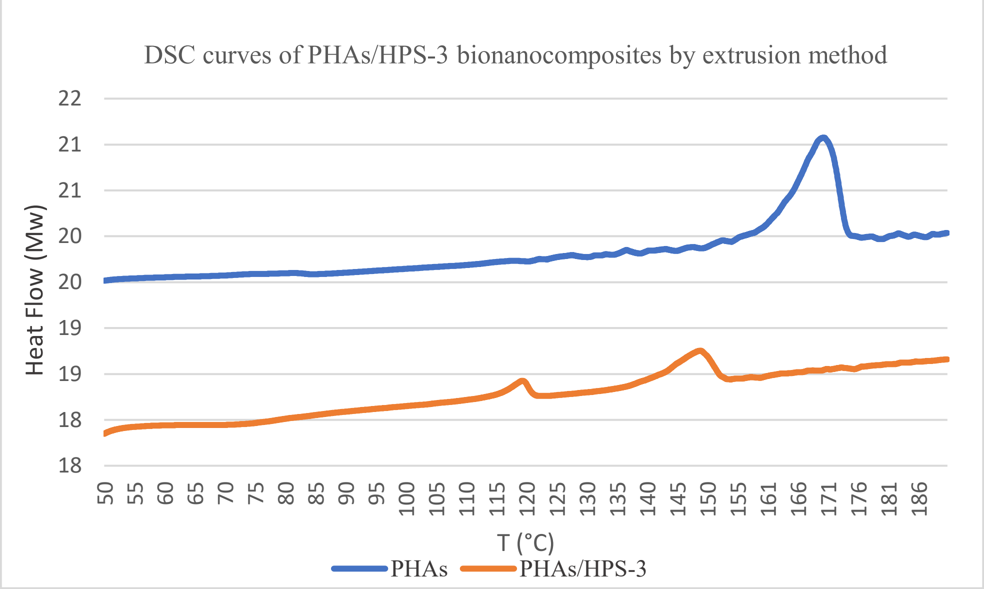


Fig. 4. DSC curves of PHAs/HPS-3 bionanocomposite by extrusion method

As seen in Figure 4 the addition of 3% HPS nanoclay to the PHAs bioblend enabled the structure to transition to a flexible form.

CONCLUSION

In this study, where sustainability and newly developing polyhydroxyalkanoate technology were discussed, PHAs bionanocomposite films were examined by solution casting and extrusion methods. Joncryl ADR 4468 was used as plasticizer, nanoclay types and metal organic frameworks containing nanofillers were used. From the mechanical and optical results, it has been determined that metal organic frameworks containing nanofillers should be used up to a maximum of 1%, while optimum results are achieved with 3% additives in nanoclay types. When the barrier results were evaluated, the inherently good OTR characteristics of P3HB4HB and P3HB showed improvement with the use of CuMOF and high purity sepiolite nanofillers compared to the reference polyethylene. The results of the study are promising in terms of recognizing material properties with the solution casting method and obtaining recipes for transition to large production with twin screw and blown film extrusion.

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